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14. ABSTRACT

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O+HCl Cross Sections and Reaction Probabilities in DSMC[1]

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Abstract. A chemical reaction model, suitable for use in the Direct Simulation Monte Carlo (DSMC) method, is developed to simulate hypervelocity collisions of an important reaction in atmospheric-jet interactions - $O(^3P)+HCl(^1\Sigma^+) \rightarrow OH(^2\Pi)+Cl(^2P)$. The model utilizes the Quasi-Classical Trajectory (QCT) method with two potential energy surfaces (PES), new benchmark triple A'' and A' surfaces[1] and London-Eyring-Polanyi-Sato (LEPS) PES.[2] The sensitivity of the flow to the fidelity of the chemical model is investigated for the new QCT-derived model and the widely used Total Collision Energy (TCE) model of Bird.[3] The adequacy of the total collision cross section is also considered, and to obtain accurate collision cross sections, the Dynamic Molecular Collision model of Tokumasu and Matsumoto[4] is assumed and the collision cross section is obtained by using the MD/QCT method with the aforementioned potential energy surfaces. The magnitude of the inelastic cross section is small compared to the total cross section for both PESs. Therefore, MD/QCT VHS-equivalent collision cross sections are obtained and along with the MD/QCT reaction cross sections are utilized in the full DSMC calculation of the flowfield. It is found that chemical reaction models do not affect the general flowfield, however, the OH production rate is dependent on the chemical reaction model.

INTRODUCTION

The modeling of chemically reacting flows caused by the interaction of a Reaction Control Systems (RCS) jet positioned on the side of a hypersonic rocket is a challenging problem. An interaction region between RCS jets and the rarefied, high Mach number atmosphere is formed at high altitudes and the relative velocities of the freestream atomic oxygen-plume chemical species are sufficiently high to produce chemical species that can radiate in various portions of the optical spectrum.

In our earlier work,[5, 6] a computational approach was established that ensured an accurate Direct Simulation Monte Carlo (DSMC)[7] solution that captured the changing flow physics over the range of freestream conditions from altitudes of 80-120 km and speeds of 3-8 km/s. Important features of the jet interaction are the hypervelocity chemical reactions between the jet and atmospheric species that occur for reactant conditions very different from the conditions for which the Arrhenius kinetic rates were obtained. Since HCl is present in high concentration in the propellant and chemically reactive atomic oxygen is available in large percentage in the freestream, the accurate modeling of the O+HCl reaction at hypervelocity conditions is crucial. In fact, at altitudes of 120 km and higher, O exchange with HCl was found to contribute more than 70 % of the OH produced.[5] A detailed study of the DSMC flowfield calculation at 120 km altitude for a freestream velocity of 5 km/s revealed an important problem for the reaction model of O+HCl.[5]

For hypervelocity collisions, the failure of the Total Collision Energy (TCE) chemistry model, widely used in DSMC, to produce the OH formation by O+HCl may be due to multiple factors. As was shown in Refs. [5] and [6], the translational perspective in the interaction region is much higher than 3,000 K, the maximum temperature for which shock tube data exists. In addition, the case of the TCE model requires assumptions regarding pre-collisional energy partitioning, that may be problematic for hypervelocity chemical reactions of this type. Since DSMC chemistry models require the use of the reaction probability, difficulties encountered with the TCE reaction probabilities in earlier work[5] may also be due to the failure of the Variable Hard Sphere (VHS) model or its parameters, which are usually obtained from low temperature flows. In our previous work,[8] the Molecular Dynamics/Quasi-Classical Trajectory (MD/QCT)

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modeling of the reaction and total collision cross sections was presented. The Dynamic Molecular Collision (DMC) model was used to calculate total collision cross sections, and the MD/QCT collision cross sections were compared with those of the VHS model. The reaction probability for O+HCl $\rightarrow$ OH+Cl obtained by the Quasi-Classical Trajectory (QCT) method with *ab initio* $^3A''$ potential energy surface of Ramachandran and Peterson (RP)[1] was compared with the TCE[3] reaction probability for an altitude of 120 km and a freestream velocity of 5 km/s. It was found that both MD/QCT cross sections affected the product species, OH.

In this work, the MD/QCT method is further investigated with two PESs, new benchmark triple A'' and A' surfaces[1] and LEPS potential of Persky *et al*.[2] The sensitivity of the flow to the fidelity of the chemical reaction model is investigated for the new QCT-derived model and the widely used TCE model.[3] Finally, we compare the changes observed in the DSMC simulation for the different chemical reaction models for the O+HCl reaction at 120 km altitude for a freestream velocity of 5 km/s.

MD/QCT MODELING

In our previous work, the VHS model with Bird values was used for the total collision cross section, σ_T. The VHS cross section is defined by $\sigma_T^{VHS} = \pi d^2$ with[3] $d = d_{ref}[2kT_{ref}/(\mu g^2)^\omega/\Gamma(2-\omega)]^{1/2}$, where d is the diameter of a molecule, μ is the molecular reduced mass, g is the relative velocity, and ω is the viscosity index ($\omega = \nu - 0.5$, ν is the coefficient of viscosity). Reference [7] gives $\omega = 0.375$, $d_{ref} = 4.38$ Å, and $T_{ref} = 273$ K for the O+HCl reaction.

For implementation in DSMC, it is more consistent to obtain a transport-based collision cross section as the total cross section and to convert the reaction cross section to a reaction probability, since the DSMC method already uses the VHS model viscosity-based cross section as the basis for computing the number of collisions per cell per time-step and as the basis for collision dynamics (hard-sphere isotropic scattering). In this spirit, Tokumasu and Matsumoto[4] demonstrated the use of the DMC model in the calculation of accurate viscosity cross sections for a given potential using a Monte Carlo integration method. While the integration over the impact parameter becomes infinite for the total collision cross section, those for momentum and energy transfer cross sections are finite. Therefore, the viscosity cross section was calculated first, and converted to the equivalent VHS collision cross section for each collision velocity.[4]

To calculate the viscosity cross section, σ_μ, by the Monte Carlo evaluation of an integral given by Ref. [9], relative velocity, change of HCl internal energy before and after a collision, and deflection angle, χ, are calculated from the MD/QCT method.[8] The MD viscosity cross section $\sigma_{\mu,MD}$ converges when the maximum impact parameter is selected so that the effect of potential is neglected. The equivalent VHS collision cross section is $\sigma_T = \pi d_t^2$, and the diameter for the total collision cross section can be obtained by $d_t = \sqrt{\frac{6\sigma_{\mu,MD}}{\pi \hat{g}^4}}$.

NUMERICAL FLOW MODELING TECHNIQUE

We consider a generic RCS-vehicle geometry with freestream conditions at high altitudes, hypersonic flight for a lateral side jet thrusting perpendicular to the rocket velocity vector into a near-vacuum environment (see Fig. 1). A small rocket is modeled as a blunted cone cylinder and a thruster positioned on the cylinder right after the cone-cylinder junction. The radius of the cylinder is 0.2 m, and the length from the head of the cone to the nozzle exit is 2 m. In this work, the angle of attack is zero. The entire set of the chemical reactions between thruster side jet and plume-atmospheric species includes reactions between oxygen and nitrogen species as well as ones that either produce or consume OH (see Table 1). The freestream parameters at 120 km altitude are listed in Table 2. The species mole fractions at the nozzle exit may be found in Ref. [5]. A starting surface was obtained from axisymmetric plume core-flow DSMC simulations that were performed with nonuniform nozzle exit conditions.[5, 6] The density isolines of about 6×10^{21} molecules/m^3 were taken for the starting surface of a 60-lbf (270-N) thruster. The starting surface is an oval shape with approximate x and y dimensions of 0.3 and 0.5 m. The three-dimensional DSMC calculations were implemented in the SMILE computational tool. The details of numerical parameters used in the calculations may be found in Ref. [8].

RESULTS AND DISCUSSION

Although the DSMC method requires the probability of a reaction, instead of the rate constant, the latter quantity provides a consistency check for the MD/QCT calculations presented in this work. Figure 2 presents the reaction rate constant calculated using a parallel MD code between 1,000 K and 3,000 K. The QCT(RP) and QCT(LEPS) are calculated in this work using the RP and LEPS surfaces, respectively. It is shown that the rate of Mahmud *et al*[10] used in our previous DSMC calculations is higher than both the QCT rates and the Improved Canonical Variational Theory (ICVT) rate constant of Xie *et al*.[11] While the QCT rates are slightly lower than the ICVT rate, the QCT rate constants of RP and LEPS surfaces agreed well in this temperature range. The tunneling effect, not included in the MD/QCT calculations, is more important for lower temperatures. For QCT(RP) calculations, because only the $^3A''$ surface was

used, the QCT(RP) calculations resulted in the lower reaction rate since the $^3A'$ surface contribution increases at higher temperatures.

Figure 3 shows a comparison of the distribution of the deflection angle χ for O+HCl collisions predicted by the VHS, Variable Soft Sphere (VSS), Linear Deflection Function (LDF),[12] and MD/QCT(RP) models. The MD/QCT results were calculated at $E_{int} = 2.0 \times 10^{-19}$ J and a relative velocity g of 5 km/s. For the VHS and VSS models, the deflection functions are given by $\chi_{VHS} = 2\cos^{-1}(b/d)$ and $\chi_{VSS} = 2\cos^{-1}(b/d)^{1/\alpha}$, respectively. The adjustable parameter α has a value between 1 and 2, and a value of 1.59[7] and a diameter, d, of 2.35 Å were used. The LDF model proposed by Dimpfl et al[12] defines since the deflection angle as, $\chi_{LDF}(b) = 180(1 - b/d_{LDF})$, where a value of $d_{LDF} = 2.63$ Å was chosen to match with the MD/QCT results. The LDF model shows better agreement with the MD/QCT results than the VHS and VSS models. However, the discrepancy increases between the MD/QCT results and all of the models for smaller deflection angles. Since it is difficult to define the cut-off deflection angle as may be seen in the figure, the DMC method is seen to be the most accurate method of calculating the collision cross section.

The preferred VHS values for O+HCl collisions were investigated using the DMC method. In our earlier reported results,[5, 6] a viscosity index ω of 0.25 for O and ω of 0.5 for HCl were used.[7, 13] However, although the viscosity index ω of HCl is 0.5 between 20 and 99 °C, for some gases, ω decreases as temperature increases.[13] Therefore, the VHS total cross sections obtained from a Maxwell molecule may not be accurate for higher temperatures. The parameters, ω and the reference diameter d_{ref} used in the previous DSMC calculations were mostly obtained from viscosity data in the low temperature range.[13] Figure 4 presents a comparison of the collision cross sections between the MD/QCT (RP and LEPS) and VHS models for O+HCl collision at $E_{int} = 0.5 \times 10^{-19}$ and 2.0×10^{-19} J. Both of the MD/QCT cross sections are greater than the VHS cross sections obtained from the data of Ref. [7] (Bird). The MD/QCT cross sections of the RP surface are slightly smaller than those of the LEPS surface. Therefore, if the MD/QCT VHS-equivalent collision cross sections are used, lower reaction probabilities are predicted than those that would be obtained from the VHS cross sections using the data in Ref. [7] (Bird). Also, it was found that the MD/QCT VHS-equivalent cross sections do not change significantly with changes of the HCl internal energy. Thus, the MD/QCT cross sections could be fit to the simpler VHS model. The parameters that give a good fit of the MD/QCT cross sections of both the RP and LEPS surfaces to the VHS form are listed in Table 3. It is found that $\sigma_{T,MD}^{VHS}(\text{RP})$ and $\sigma_{T,MD}^{VHS}(\text{LEPS})$ are slightly different, but both results are significantly different from the values used in our previous work.

Figures 5 and 6 show comparisons of the reaction probabilities for O+HCl $\rightarrow$ OH+Cl between the two MD/QCT results, $P_{r,MD}(\text{RP})$ and $P_{r,MD}(\text{LEPS})$, and the TCE model, $P_{r,TCE}$ at 3 km and 5 km, respectively. For the MD/QCT reaction probabilities, both reaction and collision cross sections were calculated. For the TCE model, the Xie's rate and VHS parameters of Bird were used. At 3 km/s, since the $\sigma_{T,MD}^{VHS}(\text{RP})$ is greater than the $\sigma_T^{VHS}(\text{Bird})$, the TCE model predicts reaction probabilities higher than $P_{r,MD}(\text{RP})$. The $P_{r,MD}(\text{LEPS})$ predicts higher probabilities if the HCl internal energy is greater than 1.0×10^{-19} J. However, for internal energy lower than 1.0×10^{-19} J, $P_{r,MD}(\text{LEPS})$ is dramatically lower than $P_{r,MD}(\text{RP})$ and $P_{r,TCE}$. This is because the LEPS reaction cross sections are lower for low internal energy than those of RP. The energy transfer from the translational to internal mode is predicted to be low for the LEPS potential. Thus, if the HCl initial internal energy is very low, some OH products can have the internal energy less than the zero point energy. These are unphysical, so they must be recalculated with a different impact parameter. At 5 km/s, the difference between $P_{r,MD}(\text{RP})$ and $P_{r,TCE}$ is decreased. Similarly, $P_{r,MD}(\text{LEPS})$ is higher than the other two models for the internal energy higher than about 1.7×10^{-19} J, and decreases rapidly as the HCl internal energy decreases.

The DSMC calculations were implemented for the four O+HCl chemical reaction models at 120 km altitude for a freestream velocity of 5 km/s. We designate the TCE model used with the previous rate constant[10] as case (1); the TCE model using the rate constant of Xie et al[11] as case (2); the MD/QCT reaction probability based on RP as case (3); and, the MD/QCT reaction probability based on LEPS as case (4). For the TCE models, the VHS total collision cross section with Bird's parameters was used. For cases (3) and (4), the MD/QCT reaction probability is the ratio of the MD/QCT reaction cross section to the $\sigma_{T,MD}^{VHS}$ of each potential (see Table 3), and the computed MD/QCT reaction probabilities were tabulated and used in the DSMC simulations. The difference in collision cross sections changes the number of collisions between O and HCl molecules which in turn, affects the OH production rate. The general flowfield contours may be found in Ref. [8]. Note that the change of chemical reaction models does not affect the overall flowfield. In addition, the change of the O+HCl collision cross section does not affect the overall flowfield because collisions between O and HCl are not the main collision in the flowfield (O is 18 % of the freestream and HCl is 14 % of the side jet).

Figure 7 shows the OH number density contours with a maximum OH number density of about 2×10^{16} m^{-3} with the case (2) chemical reaction rate. Figures 8 and 9 present the OH number density distributions along the $y = 8$ m line and the $x = -1.5$ m line, respectively, and a quantitative comparison between the four chemical reaction models is shown. As expected, the TCE model (1) predicts higher OH production than the MD/QCT models. With the case (2) reaction rate, the maximum OH number density is reduced by more than 50 % compared to the case (1) reaction. In the shock region, the reaction probabilities changed dramatically between cases (1) and (2). For case (1), the reaction rate results in TCE reaction probabilities greater than one (as found in our previous work) due to the high translational

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temperatures generated in the jet-atmosphere interaction. In contrast, with the rate of Xie *et al*, case (2), most of the O+HCl collisions are predicted to have a TCE reaction probability smaller than 0.4. While the MD/QCT(RP) probability, case (3), is slightly lower than for case (2), the MD/QCT(LEPS) probability, case (4), is much lower than for cases (2) or (3). There are two factors that caused the change in OH production between cases (2) and (3). The first factor is the larger O+HCl collision cross section obtained by the MD/QCT method that leads to more OH molecules being produced. The second factor is the lower MD/QCT reaction probability of RP, however, the effect of the change of collision cross sections was found to be smaller than the change of reaction probability. Thus, these two factors result in a slightly lower OH number density compared to case (2). The lowest OH production for case (4) is due to the lower reaction probability in low HCl internal energy range as is shown in Figs. 5 and 6. The reaction probabilities with the MD/QCT, cases (3) and (4), is lower than the TCE models, and more than 80 % of the reaction had the probability of lower than 0.1.

CONCLUSIONS

The DSMC method was applied to the calculation of chemically reacting flows of the interaction of a jet with a transition-to-rarefied atmosphere. The MD/QCT calculations for two PESs were performed for the O+HCl reaction. Both reaction and collision cross sections were obtained, and the sensitivity of the flow modeling to the fidelity of chemical reaction models in DSMC was assessed. From the comparison between RP and LEPS potentials, it is found that since energy transfer from translational to internal modes are low for the LEPS potential, and the LEPS reaction probability is predicted to be low for low HCl internal energies, the OH production modeled with MD/QCT(LEPS) was lower than the MD/QCT(RP) case. The LEPS potential, although much simpler and readily available than the RP surfaces are, gives significantly different results when used in the DSMC simulation. The difference in the DSMC results, in contract to the similarity in the rates (Fig. 2) is due to the high degree of nonequilibrium in the flow.

ACKNOWLEDGMENTS

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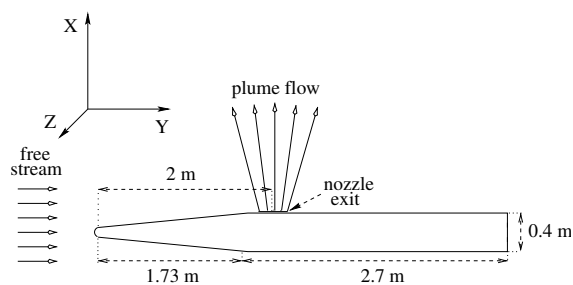
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FIGURE 1. Schematic of the flow.

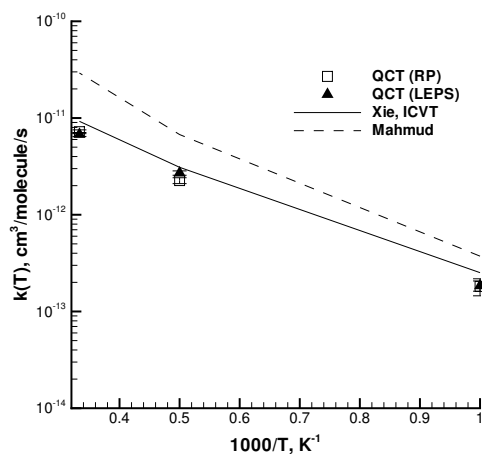**FIGURE 2.** Reaction rate constant for O+HCl → OH+Cl as a function of temperature. The QCT(RP) and QCT(LEPS) are calculated in this work.
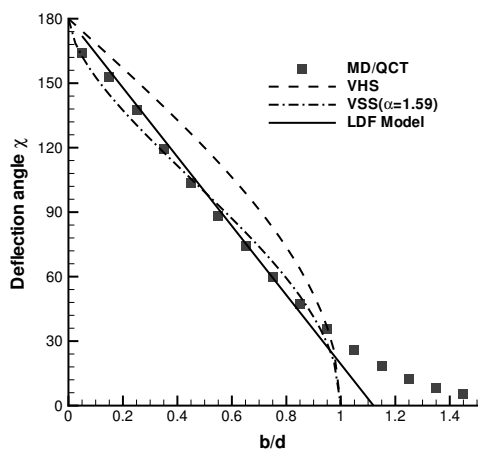

FIGURE 3. Comparison of distributions of the deflection angle χ for O+HCl collisions predicted by the VHS, VSS, LDF models, and MD/QCT. The MD/QCT results were calculated at $E_{int} = 2.0 \times 10^{-19}$ J and a relative velocity of 5 km/s.
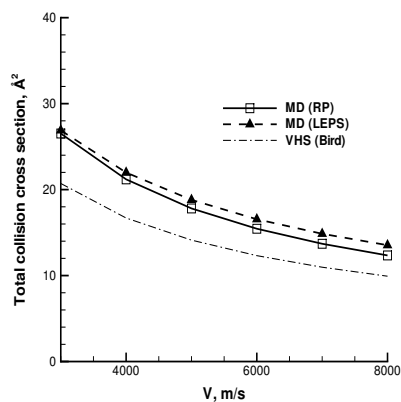

FIGURE 4. Comparison of total collision cross sections between MD/QCT (RP and LEPS) and VHS models for O+HCl collision.
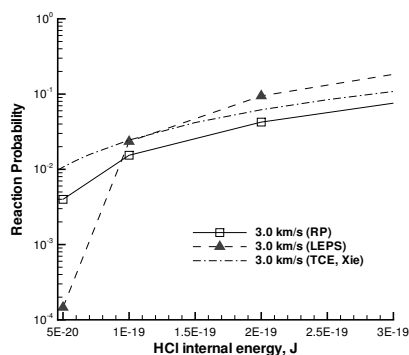
FIGURE 5. Comparison of the reaction probability calculated by using the reaction cross section divided by MD/QCT total collision cross section (σ_T(MD)): Reaction probabilities as a function of the reactant internal energy at 3 km/s.
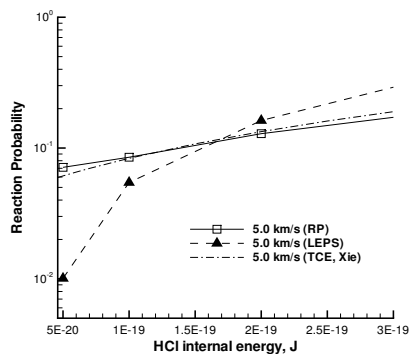

FIGURE 6. Comparison of the reaction probability calculated by using the reaction cross section divided by MD/QCT total collision cross section (σ_T(MD)): Reaction probabilities as a function of the reactant internal energy at 5 km/s.

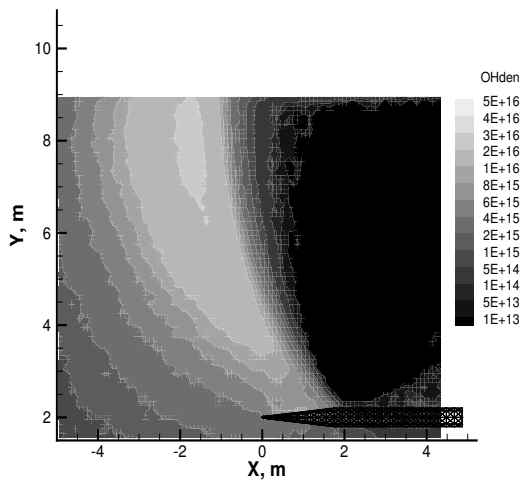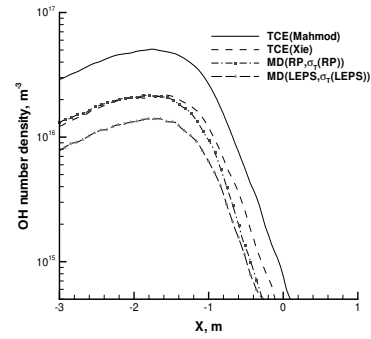**TABLE 1.** Freestream-plume species reactions for OH production

Reaction	A, m^3/s	n	E_a, $\times 10^{-19}$ J
$H_2O+N_2 \rightarrow OH+H+N_2$	5.81×10^{-15}	0.00	7.314
$H_2O+O_2 \rightarrow OH+H+O_2$	1.13×10^{-7}	-1.31	8.197
$H_2O+O \rightarrow OH+H+O$	1.13×10^{-7}	-1.31	8.197
$H_2O+O \rightarrow OH+OH$	1.13×10^{-16}	0.00	1.275
$H+O_2 \rightarrow OH+O$	1.66×10^{-16}	0.00	1.061
$O+H_2 \rightarrow OH+H$	3.12×10^{-16}	0.00	0.952
$OH+Cl \rightarrow O+HCl$	3.10×10^{-27}	2.91	0.070
$O+HCl \rightarrow OH+Cl(Mahmud)$[10]	5.60×10^{-27}	2.87	0.244
$O+HCl \rightarrow OH+Cl(Xie)$[11]	1.70×10^{-22}	1.485	0.408

TABLE 2. Freestream parameters

Parameter	120 km
Temperature, K	354
Number density, molec/m^3	4.73×10^{17}
O$_2$ mole fraction, %	9
N$_2$ mole fraction, %	73
O mole fraction, %	18

TABLE 3. VHS parameters for O+HCl

Method	ω	d_{ref}, Å	T_{ref}, K
Bird	0.375	4.38	273
QCT(RP)	0.390	3.9	1000
QCT(LEPS)	0.350	3.8	1000

FIGURE 8. Comparison of OH number density (molecule/m^3) at $y = 8$ m for four chemical reaction models at 120 km altitude for freestream velocity of 5 km/s.

FIGURE 7. OH number density (molecule/m^3) contours with the rate of Xie *et al* (TCE) at 120 km altitude for freestream velocity of 5 km/s. Area shown is 7.4×7.5 m.
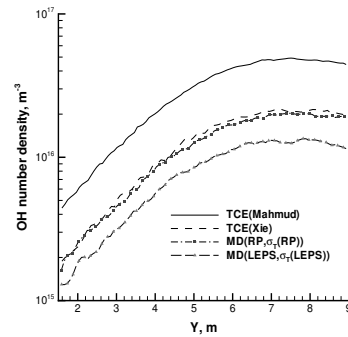
FIGURE 9. Comparison of OH number density (molecule/m^3) at $x = -1.5$ m for four chemical reaction models at 120 km altitude for freestream velocity of 5 km/s.